

## Properties of Lactoprene BN-12.5, a Copolymer of Butyl Acrylate and Acrylonitrile, and Its Vulcanizates

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The knowledge gained in the development of Lactoprene EV, a copolymer of ethyl acrylate and chloroethyl vinyl ether, was used in developing another synthetic rubber designated Lactoprene BN, a copolymer of butyl acrylate and acrylonitrile. It may be prepared by the conventional polymerization techniques to yield a tack-free white product. The rubber can be handled on the ordinary rubber processing equipment and it bands readily when the rolls of the rubber mill are maintained at 150°F. By the proper choice of curatives, the vulcani-

zates exhibit outstanding resistance to heat and hot lubricating oils. The water resistance of the vulcanizates is significantly improved over that of Lactoprene EV, and the brittle points are substantially lower. This paper describes the properties of the vulcanizates obtained from a copolymer prepared from a monomer mixture of 87½% butyl acrylate and 12½% acrylonitrile. The properties of several commercially produced synthetic rubbers are included in this paper for purposes of comparison.

SEVERAL years ago this Laboratory published several papers (1-8) describing methods of preparing polymers and copolymers of ethyl acrylate which could be vulcanized with curatives frequently employed for diene rubbers. These early papers also summarized the chemical and physical properties of the vulcanizates. The most promising copolymer, ethyl acrylate and chloroethyl vinyl ether, designated Lactoprene EV, is now commercially available as Hycar PA-21.

The early studies demonstrated that conventional compounding facilities can be employed to incorporate the reinforcing agents and curatives. It was shown that several curatives and accelerators commonly used in the

vulcanization of natural rubber and GR-S can be used with advantage with the saturated acrylic rubbers. However, an amine, Trimene Base, and sulfur recipe was found to impart outstanding resistance to dry heat. In addition, the low volume swelling of these vulcanizates in lubricating oils suggests many applications such as O-rings, gaskets, oil seals and similar mechanical goods.

These vulcanizates of Lactoprene EV exhibit certain limitations. For example, the brittle point, about +12°F., is relatively high and the swelling in water at 100°C., about 50% in 48 hours, is excessive. In an effort to correct these deficiencies the copolymers of butyl acrylate and acrylonitrile were investigated. A previous paper (9) summarized the preliminary data on several butyl acrylate-acrylonitrile compositions. The present paper describes the recently completed evaluation

Note: The Eastern Regional Research Laboratory is one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

TABLE I — OSMOTIC PRESSURE MOLECULAR WEIGHTS AND VISCOSITIES OF THE LACTOPRENE BN-12.5 COPOLYMERS

Sample No.	Molecular Weight <sup>a</sup>	Intrinsic Viscosity <sup>a,b</sup>
19 Q 1B1 <sup>c</sup>	1,760,000	5.46
T-302 <sup>d</sup>	901,000	—
T-306 <sup>d</sup>	780,000	3.38

(a) Acetone used as solvent. (b) Concentration in g./100 ml. (c) Prepared in Government Laboratories at the University of Akron. (d) Prepared in the laboratory.

of the copolymer prepared from a monomer composition of 87½% butyl acrylate and 12½% acrylonitrile. This material has been designated Lactoprene BN-12.5 in accordance with the practice of the acrylic rubber development of this Laboratory. The number following the name indicates the amount of acrylonitrile in the monomer mixture.

### Preparation and Characterization of the Raw Rubber

The procedure and the recipe employed for preparing these copolymers is substantially the same as that described in the previous publication (9). A paper describing in greater detail the preparation of acrylic ester-acrylonitrile copolymers has recently been published (10). The material used in this evaluation study was part of a pilot plant batch prepared in the Government Laboratories of the Office of Synthetic Rubber operated by the University of Akron. The recipe employed for this material was similar to those used in laboratory batches; however, a substantial amount of prefloc formed in the large reactor which did not form in the laboratory-prepared samples.

Acrylic monomers, because of their reactive double bond, polymerize readily into high molecular weight polymers. Frequently, insoluble products are formed which nevertheless can be compounded in the conventional manner. The solution polymerization, using benzene in moderate concentrations as a solvent, always yields a soluble polymer with high molecular weight.

The emulsion method for the polymerization process frequently results in a polymer containing a low percentage of insoluble gel. Table I illustrates the osmotic pressure molecular weights and intrinsic viscosities for several polymers.

### Compounding and Curing

Since these polymers are substantially saturated, the vulcanization process may not be the same as for the diene type rubbers. However, many curatives used in the vulcanization of these latter materials are also operative with acrylic rubbers. The experience gained in the development of Lactoprene EV indicated that the acrylic rubbers cured with an amine and sulfur should have good resistance to dry heat. These conclusions were substantiated in this study and Table II illustrates the recipes used in the evaluation of Lactoprene BN-12.5.

As with Lactoprene EV but in contrast to many diene polymers no initial breakdown is required. Furthermore, these acrylic copolymers band readily on the mill. There is a tendency for the materials to adhere to the rubber compounding rolls prior to the addition of the carbon black. In order to reduce the tendency for the stock to stick to the back roll, stearic acid is incorporated. Usually one part of stearic acid suffices and the rubber then remains on the front roll during compounding. In this study, however, we have employed an internal mixer for incorporating the filler and stearic acid. This is convenient since premastication is not necessary and the mixing schedule is shortened.

The following compounding scheme was found to be satisfactory for Lactoprene BN-12.5: The raw rubber is placed in the Banbury mixer maintained at 180°F. It is run at low speed (95 r.p.m. on the "Midget") for about one-half minute. The carbon black and stearic acid which have been superficially mixed are then added and the mixing continued for an additional two minutes at low speed. Mixing is continued for another three minutes at high speed (190 r.p.m. on the "Midget"). The compounded stock may tend to adhere to the mixer blades if the temperature rises too high. However, it can be readily removed by

TABLE II—THE EFFECT OF VARIOUS RATIOS OF TRIETHYLENE TETRAMINE AND SULFUR ON THE TENSILE PROPERTIES OF LACTOPRENE BN-12.5 VULCANIZATES CONTAINING FURNEX CARBON BLACK

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
Lactoprene BN-12.5 .....	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Stearic acid .....	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Semi-reinforcing furnace black (Furnex) .....	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Sulfur .....	0	0.25	0.5	0.75	0	0.25	0.5	0.75	1	1	1	1	1	1	1	1	1
Triethylene tetramine ....	0.75	0.75	0.75	0.75	1	1	1	1	0.5	1	1.5	2	1	1	1	1	2
Initial Properties Cured 60 Minutes at 298°F.																	
Tensile strength, p.s.i. ....	790	1350	1380	1380	980	1310	1460	1490	N	1400	1370	1290	1360	1400	1370	1380	1390
Ultimate elongation, %...	780	480	480	490	650	310	300	330	O	330	230	120	270	290	290	300	420
Shore A hardness (30 sec.)	36	44	48	46	40	54	55	55	C	330	230	120	270	290	290	300	420
Modulus at 100% .....	90	160	180	190	130	260	310	330	U	55	60	71	59	60	59	60	46
200% .....	230	390	480	480	290	740	860	830	R	250	420	990	350	380	380	400	180
									E	720	1200	—	940	950	930	930	420
Aged 72 Hours at 350°F.																	
Tensile strength, p.s.i. ....	320	1200	1380	1450	460	1160	1390	1390	—	1300	1390	1650	1320	1390	1300	1350	710
Ultimate elongation, %...	130	250	240	250	130	160	140	140	—	130	90	50	100	100	100	110	70
Shore A hardness (30 sec.)	60	64	62	62	61	68	76	76	—	73	80	91	80	80	79	80	75
Modulus at 100% .....	250	390	490	450	360	640	1000	940	—	1020	—	—	1300	1390	1300	1330	—

[illegible]

TABLE IV—THE EFFECT OF VARIOUS RATIOS OF TRIETHYLENE TETRAMINE AND SULFUR ON THE TENSILE PROPERTIES OF LACTOPRENE BN-12.5 VULCANIZATES CONTAINING P-33 AND WYEX CARBON BLACKS

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Lactoprene BN-12.5	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Fine thermal furnace black—P-33	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Easy processing channel black—Wyex	1.0	1.0	1.0	1.0	0	0.5	1.0	1.0	1.0	1.5	2	2.5	2	2	2	2
Sulfur	0.5	1.0	1.5	2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Triethylene tetramine	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Initial Properties Cured 60 Min. at 298°F.																
Tensile strength, p.s.i.	N	1520	1640	1550	1070	1540	1380	1460	940	1250	1480	1580	1200	1220	1420	1480
Ultimate elongation, %	O	440	310	190	630	340	370	390	700	450	300	240	460	420	240	260
Shore A hardness (30 sec.)	C	53	63	71	45	60	59	59	50	60	70	73	56	64	68	68
Modulus at 100%	U	220	390	720	170	370	280	290	280	430	630	810	410	490	780	780
Modulus at 200%	R	590	980	—	310	800	620	660	540	790	1140	1390	710	780	1290	1290
Aged 72 Hours at 350°F.																
Tensile strength, p.s.i.	E	1190	1310	1510	800	1140	1190	1230	890	1050	1300	1390	670	1070	1380	1340
Ultimate elongation, %	—	190	110	60	180	120	150	150	220	170	110	80	110	160	90	90
Shore A hardness (30 sec.)	—	70	82	91	68	82	80	80	69	78	85	90	72	80	86	86
Modulus at 100%	—	610	1300	—	460	1000	840	880	600	820	1250	—	670	880	—	—

cations D-412-41 using a die similar to Die D except that the reduced section was 1/4-inch wide.

Tables II, III and IV show the effect of various ratios of sulfur and triethylene tetramine on the initial tensile properties with four carbon black fillers—Furnex, Philblack O, P-33 and Wyex. The carbon black loadings used in this study were restricted to those illustrated in the tables. A previous inspection showed that these carbon black concentrations gave adequate reinforcement; however, other carbon black loadings may result in stocks superior to those described in this paper.

These tables also show the change in properties on heat aging in an air convection oven. As can be seen, it is possible to obtain satisfactory vulcanization in the absence of sulfur but on exposure to temperatures of 350°F. there is an inordinate decrease in the tensile strength of the vulcanization regardless of the type of carbon black filler used. See for example Table II recipes A, E and Q; Table III recipes A, E and I; and Table IV recipes E and M.

The incorporation of relatively small amounts of sulfur, for example Table II recipes B and F, yields vulcanizates which retain virtually completely their

original tensile strength on aging. For those stocks containing Philblack O (Table III) satisfactory cures are obtained with only 0.5 parts of triethylene tetramine. Tables II, III and IV show that high concentrations of triethylene tetramine should be avoided for the best retention of tensile properties and furthermore that high concentrations of sulfur apparently do not impart any additional resistance to heat.

It should be noted, however, that low concentrations of sulfur accelerate the vulcanization process. This is borne out by comparing recipes A and B in Table II. The addition of only 0.25 part of sulfur while the triethylene tetramine concentration is constant at 0.75 part increases the tensile strength from 790 to 1350 p.s.i. while the elongation decreases from 780 to 480%. By compromising between the best initial tensile properties and the best heat aged tensile properties several recipes were chosen for extensive evaluation. These recipes are: Table II G and J, Table III F and U, and Table IV B and K. This provided two recipes containing Furnex, two recipes containing Philblack O, and one recipe each for P-33 and Wyex blacks. Philblack O loaded stocks containing a minimum of curative, 0.5 part of triethylene tetramine in recipes B, C, and D in Table III, have

TABLE V—EFFECT OF CURE TIME ON INITIAL PROPERTIES

Sample	G(II)*	G(II)	G(II)	G(II)	J(II)	J(II)	J(II)	J(II)	F(III)	F(III)	F(III)	F(III)
Cure Time (mins.) at 298°F.	15	30	60	120	15	30	60	120	15	30	60	120
Tensile strength, p.s.i.	1430	1500	1500	1540	1470	1470	1470	1540	1690	1790	1670	1620
Ultimate elongation, %	320	270	250	200	320	260	260	190	380	330	280	220
Modulus at 100%	270	340	370	600	280	380	360	690	380	430	530	720
Shore A hardness (30 sec.)	54	58	60	62	54	56	60	63	60	65	69	71
Sample	U(III)	U(III)	U(III)	U(III)	B(IV)	B(IV)	B(IV)	B(IV)	K(IV)	K(IV)	K(IV)	K(IV)
Cure Time (mins.) at 298°F.	15	30	60	120	15	30	60	120	15	30	60	120
Tensile strength, p.s.i.	1560	1750	1790	1840	1430	1380	1460	1570	1640	1760	1600	1720
Ultimate elongation, %	420	390	310	270	320	350	290	270	340	350	420	270
Modulus at 100%	360	390	480	590	380	400	490	600	480	500	460	740
Shore A hardness (30 sec.)	64	65	68	74	58	64	66	66	62	64	70	70

\* The letter indicates the recipe for preparing the vulcanizate and the number in parentheses indicates the table where the recipe may be located.

outstanding heat resistance as exemplified by the fact that the vulcanizates still exhibited better than 450% elongation after aging for 72 hours at 350°F. Since many of the small laboratory batches of Lactoprene BN-12.5 did not yield satisfactory cures with this low concentration of triethylene tetramine it was decided to use higher amine concentrations in the evaluation study.

Table V shows the change in the initial tensile properties of the vulcanizates obtained with the selected recipes for curing times from 15 minutes to 120 minutes. These data show that for the various recipes 15 minutes at 298°F. results in vulcanizates which are sufficiently cured for many applications. In this study, therefore, the vulcanizates of Lactoprene BN-12.5 were cured for 15 minutes at 298°F.

### Comparison with Other Synthetic Rubbers

For a proper comparison of the properties of Lactoprene BN-12.5 vulcanizates with other commercially available rubbers it was deemed advisable to actually evaluate the latter vulcanizates with those of Lactoprene BN. The following rubbers were included in this study: Paracril 18-80, Hycar OR-15, Hycar OR-25, Perbunan 26, and Hycar PA-21. The recipes and processing techniques employed were usually those recommended by the manufacturer for heat resistant applications. These recipes are presented in Table VI along with the initial tensile properties of the cured test slabs. These vulcanizates were subjected to the same experimental conditions and at the same time as the acrylic elastomer.

### Resistance to Dry Heat

An intensive study of the resistance to dry heat of Lactoprene BN-12.5 vulcanizates was undertaken. The deterioration due to heat was studied in both an air-convection oven at 300° and 350°F. and in an enclosed system at 350° and 400°F. The change in the tensile properties such as tensile strength, elongation, modulus, and durometer hardness was observed over extended periods of time. Dumbbell samples cut from the test slabs were either hung in the oven or hung on racks in sealed containers. No attempt was made to remove or displace the residual air in the containers. Periodically

TABLE VI—RECIPES AND INITIAL TENSILE PROPERTIES OF COMMERCIAL RUBBERS USED IN THIS STUDY

Recipe	Para-cril 18-80	Hycar OR-25	Hycar OR-15	Perbu- nan 26	Hycar PA-21
Rubber .....	100	100	100	100	100
Stearic acid .....	1	—	1	1	1
Furnex .....	54	70	60	54	50
Agerite Resin D.....	2	2	—	2	—
Methyl Tuads .....	3	2	—	3	—
Santocure .....	—	1	—	—	—
Altax .....	—	—	1.5	—	—
Zinc oxide .....	5	5	5	5	—
Sulfur .....	—	0.5	1.5	—	0.5
Trimene Base .....	—	—	—	—	3
Cure Time (Min.)...	60	45	30	60	45
Temperature (°F.) ..	287	310	310	287	310
Initial Properties					
Tensile strength, p.s.i.	2120	2550	2370	2140	1370
Elongation, % .....	510	260	310	550	190
Modulus at 100%, p.s.i.	210	740	510	200	700
Shore A hardness (30 sec.) .....	60	75	71	63	69

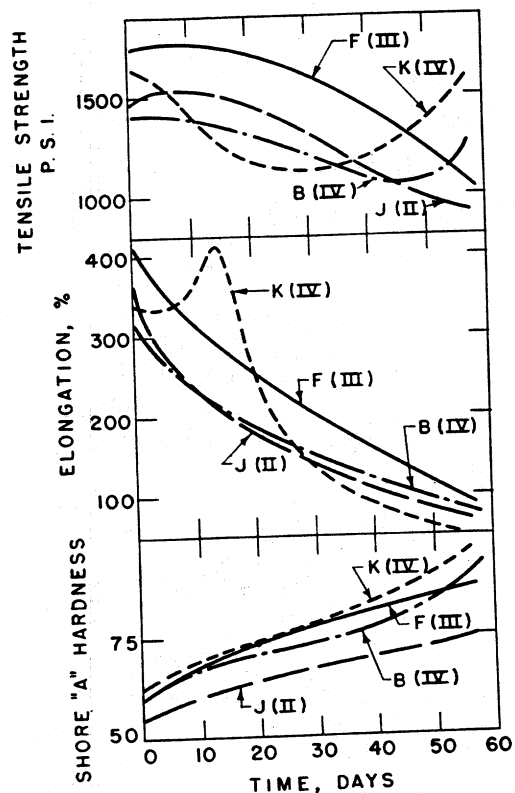


FIG. 1—Heat aging of Lactoprene BN-12.5 vulcanizates in an air-convection oven at 300°F.

samples were removed for testing. The commercial rubbers were evaluated similarly in the air convection oven at 300°F. and at 350°F. in the sealed containers.

Figure 1 shows the change of the tensile strength, elongation and hardness of the Lactoprene BN-12.5 vulcanizates, containing four different reinforcing agents, to dry heat at 300°F. for various times up to 56 days. Both the Furnex and Philblack O-loaded stocks show essentially a gradual lowering of tensile strength and elongation and a gradual increase in durometer hardness. At the end of 56 days at 300°F. the stocks still retained tensile strengths in excess of 900 p.s.i. and elongations better than 70%. The durometer hardness of the two stocks increased from an initial value of 55 and 60, respectively, to 75 and 85, respectively, at the end of 56 days' exposure. The P-33-loaded stocks show a similar decrease in tensile strength and elongation and a gradual increase in hardness. The Wyex stocks, however, showed a rather rapid decrease in tensile strength which remained approximately constant for about three weeks and then a rapid increase in tensile strength. The tensile strength of the Wyex stocks was initially 1640 p.s.i. and decreased to about 1120 p.s.i. at the end of 35 days; however, at the end of 56 days the tensile strength increased to 1760 p.s.i. The elongation of the Wyex stocks exhibited an initial elongation of 340% and increased to 410% in 14 days; subsequently, the elongation decreased most rapidly of the variously loaded stocks to a value of 50% at the end of the test. In addition, the Wyex stocks showed the greatest increase in hardness of the four reinforcing agents studied.

The change in the physical properties of the other rubbers studied in the air-convection oven at 300°F. are shown in Figure 2. With the exception of Hycar PA-

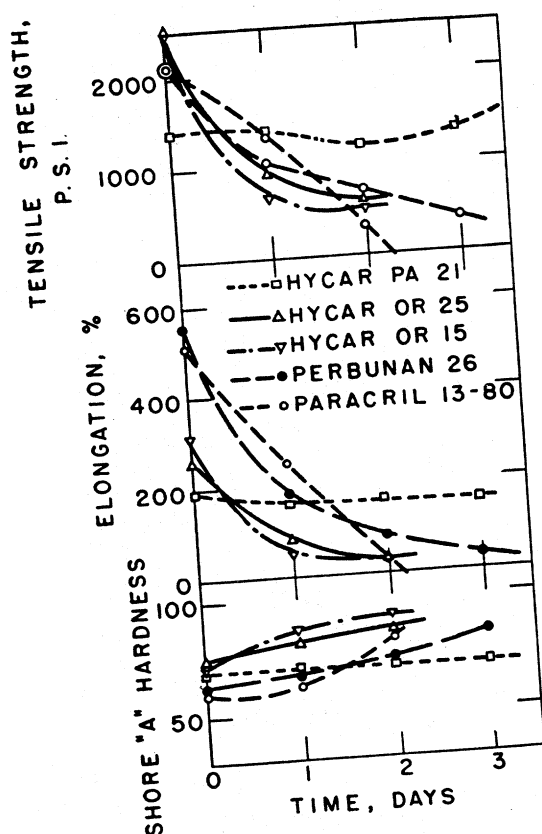


FIG. 2—Heat aging of commercial rubbers in an air-convection oven at 300°F.

21, all the samples had deteriorated at the end of four days to such an extent that they could not be tested.

At an even higher temperature, 350°F. in the air-convection oven, the Lactoprene BN-12.5 vulcanizates exhibited the change in physical properties shown in Figure 3. The Wyex-loaded vulcanizates showed the greatest decrease in tensile strength while the Furnex, Philblack O, and P-33-loaded vulcanizates showed very little change at the end of seven days. The elongations of these vulcanizates decreased to about 100% at the end of the exposure while the durometer hardness of the vulcanizates increased about 20 points above the initial hardness values.

Since the exposure of the samples to heat in the air-convection oven does not approach the actual service conditions where these materials may find ultimate utility, such as gaskets, oil seals, and O-rings, the vulcanizates were placed in sealed containers and exposed for various lengths of time to temperatures of 350° and 400°F. It was felt that the above applications confine the samples of rubber so that air oxidation or the loss of oxidation inhibitors is minimized. Therefore, these conditions are more nearly simulated by exposing the samples to heat in an enclosed system.

Figure 4 illustrates the change in some of the tensile properties of the vulcanizates on exposure in sealed vessels to temperatures of 350°F. As can be seen, there is little change in either the tensile strength or elongation in the two differently reinforced stocks in 28 days while there is only a slight increase in the hardness values. There is materially less change in these tensile data than those obtained from samples exposed to 300°F. in the air-convection oven (see Figure 1).

Figure 5 illustrates the effect of 350°F. aging for

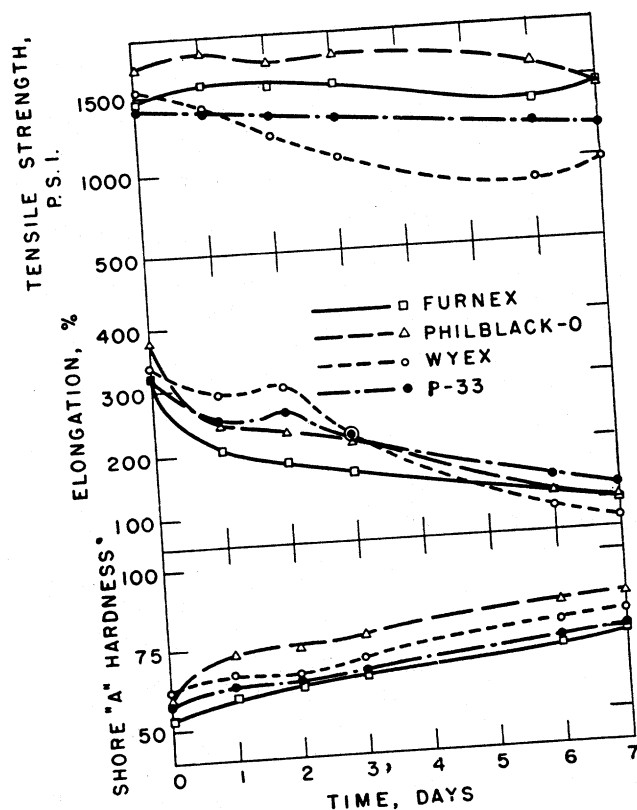


FIG. 3—Heat aging of Lactoprene BN-12.5 vulcanizates in an air-convection oven at 350°F.

the commercial rubbers under identical conditions. At the end of 15 days all the samples exhibited elongations of 50% and were in general so brittle that they could not be clamped in the tensile tester. The length of time to reach this state of deterioration was again consid-

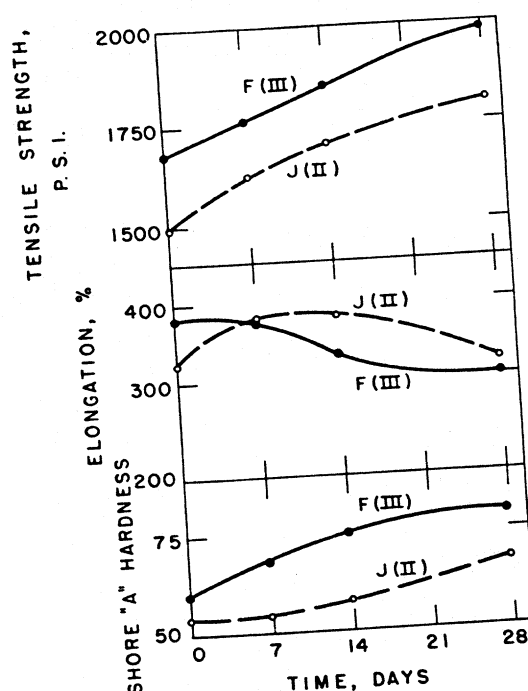


FIG. 4—Heat aging of Lactoprene BN-12.5 vulcanizates in sealed containers at 350°F.

erably extended from that obtained at 300°F. in the air-convection oven (see Figure 2).

The effect of aging of the Lactoprene BN-12.5 vulcanizates at 400°F. in a sealed system is shown in Figure 6. The change in the tensile strength, elongation, and hardness are illustrated for samples exposed to 400°F. for various lengths of time in sealed vessels up to 28 days. For comparison, the data obtained for a silicone rubber vulcanizate is included. The Lactoprene BN stocks still retained tensile strengths better than 1300 p.s.i. and elongations somewhat greater than 150% after 28 days' exposure. The durometer hardness values increased about 20 points. The silicone rubber, designated G-E 12660 (kindly supplied by the General Electric Company), shows a much less percentage change in the tensile properties; however, its tensile strength and elongation are substantially lower than the acrylate-acrylonitrile vulcanizates.

### Resistance to Hot Lubricating Oils

An intensive study of the oil resistance of Lactoprene BN-12.5 vulcanizates was also undertaken. The volume change as measured by the percent change in volume of rectangular specimens suspended in the ASTM Oils Numbers 1, 2 and 3 and a commercial automatic transmission oil at 300° and 350°F. was determined over a period of 28 days. In addition, the change in the tensile properties of dumbbells suspended in the hot oils was also determined. The latter oil, because of its exposure to extremely high temperatures, contains a number of additives to increase its useful life; unfortunately, many of these additives are extremely deleterious to most rubbers. This oil was included therefore to observe its effect on the Lactoprene BN vulcanizates.

It should be borne in mind that under the conditions of this test two effects are operating simultaneously. One is the effect of the elevated temperature upon the deterioration of the rubber which has been described in the previous section. The specimens immersed in the

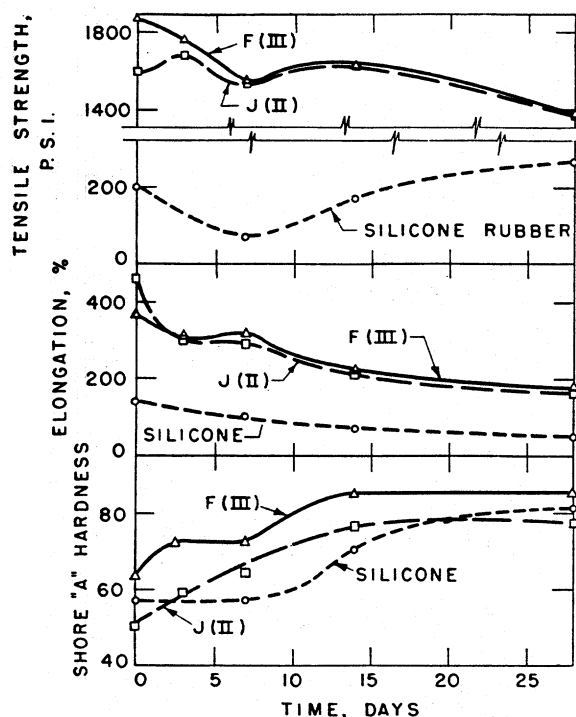


FIG. 6—Heat aging of Lactoprene BN-12.5 vulcanizates and a silicone rubber in an enclosed system at 400°F.

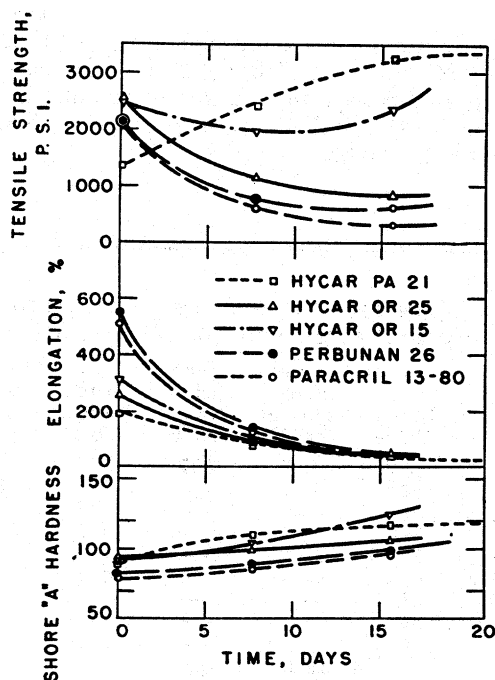


FIG. 5—Heat aging of commercial rubbers in sealed containers at 350°F.

hot lubricating oils may be considered in a similar environment as those samples exposed to dry heat in the enclosed systems. However, the rate of chain scission and cross-linking in the oils, in comparison to these rates in the simple heat aging, is complicated by the additional action of the oil and its decomposition products on the vulcanizates. The change in tensile properties with immersion time in hot oils was used in this investigation as a criterion of the deterioration of the vulcanizates due to the heat and oil. The second effect is the volume swelling of the rubber in the hot oils. This is a thermodynamic property depending upon the number of cross-links and the polymer-oil interaction. It is beyond the scope of this paper to discuss the thermodynamic properties of this acrylic rubber.

Test dumbbells were prepared from the same test slabs as used in the heat aging studies. Rectangles 1-inch x 1½-inch cut from these slabs were used in the volume swelling determinations. This latter determination was performed following the procedure described in ASTM designation D471-46T. Furthermore, the oil was discarded every seven days and then replaced with fresh oil.

The percent volume increase and tensile data for four commercial rubbers are presented in Table VII. The samples were immersed in the lubricating oils up to 28 days at 300°F. The data in Table VII show some of the initial tensile properties of the vulcanizates and the tensile properties and volume swelling for two immersion times. At the end of 28 days the Lactoprene rubbers showed an increase in volume swelling of about 2% in ASTM Oil No. 1 between 9 and 12% in ASTM Oil No. 2, between 27 and 36% in ASTM Oil No. 3, and between 11 and 16% in the commercial automatic transmission fluid. Furthermore, the tensile strength and elongations of the acrylate vulcanizates were consistently high, showing negligible deterioration un-



TABLE VII—VOLUME SWELLING AND TENSILE PROPERTIES OF VULCANIZATES IMMERSSED IN VARIOUS OILS AT 300° F.

Sample Designation	Initial Properties		Length of Time Immersed	ASTM No. 1 Oil			ASTM No. 2 Oil			ASTM No. 3 Oil			Commercial Automatic Transmission Fluid		
	T.S. <sup>b</sup>	E. <sup>c</sup>		T.S.	E.	H.	T.S.	E.	H.	T.S.	E.	H.	T.S.	E.	H.
J(II) <sup>a</sup>	1580	420	52	1780	230	64	1590	210	60	1130	190	55	1450	220	56
				1290	320	62	1230	340	48	840	330	44	1250	360	50
F(III)	1690	430	61	2040	260	70	1900	250	69	1260	250	57	1620	270	61
				1570	300	71	1500	340	62	960	340	50	1400	360	61
B(IV)	1380	260	62	1250	330	65	1140	420	60	850	430	55	1100	500	57
				1340	250	69	1100	350	63	780	370	55	1060	390	61
K(IV)	1570	320	66	1550	230	70	1350	250	65	920	200	60	1250	280	63
				1460	220	76	1330	260	65	840	250	57	1260	290	61
Hycar OR-25...	2550	260	75	2380	220	74	1470	160	75	750	130	68	720	100	71
				1890	150	76	560	80	74	480	100	71	720	100	71
Hycar PA-21...	1370	160	69	1390	140	79	1580	150	76	1370	180	67	1470	140	76
				1510	110	81	1540	130	79	1410	160	75	1470	140	76
Hycar OR-15...	2470	310	71	2760	230	78	820	90	76	610	100	75	690	90	80
				1370	110	80	—1.6	B L A N K	—	—	B L A N K	—	—	—	—
Perbunan 26...	2140	550	63	2170	390	59	1810	350	54	1210	350	45	180	120	47
				840	170	62	400	130	55	410	140	51	180	120	47

(a) Symbol denotes the table in paper and recipe for preparing vulcanizate.

(b) Tensile strength in lbs. per sq. in.

(c) Percent elongation.

(d) Shore A hardness (30 sec.).

(e) Volume swelling, %.

der these conditions. The commercial rubbers tested, with the exception of Hycar PA-21, exhibited a substantial decrease in tensile properties at the end of the test, particularly in the automatic transmission fluid.

Table VIII summarizes the volume swelling and tensile data obtained on the vulcanizates immersed in ASTM Oils Nos. 1 and 2 at 350°F. At this temperature, as above, the samples were immersed up to 28 days and data are shown for two immersion times. Only two Lactoprene vulcanizates were employed in this study at this temperature, sample numbers J (II) and F (III), loaded with Furnex and Philblack O, respectively. The Lactoprene rubbers showed very little deterioration at this temperature since both the tensile strengths and elongations remained fairly high up to 28 days. On the other hand, the elongations of the commercial rubbers (including Hycar PA-21) were extremely low at the end of the test.

### Compression Set

Low compression set is extremely important for rubber vulcanizates to be employed in applications such as gaskets, O-rings, and similar mechanical goods. Since acrylate rubbers such as Lactoprene EV (Hycar PA-21) are being used in such applications, it is anticipated that these new acrylate-acrylonitrile rubbers should also provide material for similar mechanical specialties. Table IX summarizes the compression set data obtained on the four representative Lactoprene BN-12.5 vulcanizates and the four comparative rubbers tested at 250°F. for 70 hours.

The second column in the table shows the results obtained on the unaged vulcanizates. It shows that the compression set is inordinately high for the four Lactoprene BN-12.5 and Hycar PA-21 vulcanizates while two of the comparative rubber vulcanizates are low. However, since the Lactoprene rubbers have outstanding resistance to dry heat they may be conveniently aged or tempered in an air-convection oven for a short time prior to the compression set determination. This is common practice these days in the fabrication of certain specialty rubbers. This practice is unsatisfactory with most other rubbers because of their relatively poor heat resistance. The table shows that aging the vulcanizates substantially improves the compression set and that tempering for 24 hours at 350°F. in an air-convection oven is approximately the optimum condition, since longer exposure to this high temperature will affect the useful life of the rubber.

TABLE IX—COMPRESSION SET<sup>a</sup> OF THE LACTOPRENE BN-12.5 VULCANIZATES AND COMMERCIAL RUBBERS

Sample Designation	Initial Value	Tempered 2 hrs. at 300°F.	Tempered 2 hrs. at 350°F.	Tempered 24 hrs. at 300°F.	Tempered 24 hrs. at 350°F.
J(II) <sup>b</sup>	80.7	56.7	45.7	37.7	29.7
F(III)	92.1	73.7	—	51.5	40.4
B(IV)	77.6	—	—	49.5	47.9
K(IV)	86.8	—	—	59.5	54.3
Hycar OR-25	39.0	—	—	—	—
Hycar PA-21	93.4	—	—	42.1	—
Hycar OR-15	83.1	—	—	—	—
Perbunan 26..	34.1	—	—	—	—

(a) ASTM D-395-47-T, Method B. (b) Symbol denotes recipe and table for preparing vulcanizate.



TABLE X—TENSILE PROPERTIES OF LACTOPRENE BN-12.5 VULCANIZATES AND COMMERCIAL RUBBERS

Sample Designation	Initial Properties			Tensile Properties (Tempered 24 hrs. at 300°F.)			Tensile Properties after Aging 28 Days in Water at 212°F.					
	Untempered						Untempered			(Tempered 24 hrs. at 300°F.)		
	T.S. <sup>b</sup>	E. <sup>c</sup>	H. <sup>d</sup>	T.S.	E.	H.	T.S.	E.	H.	T.S.	E.	H.
J(II) <sup>a</sup> .....	1600	460	50	1700	300	56	1020	130	62	800	170	58
F(III) .....	1880	370	63	1930	250	67	1330	130	72	800	160	60
B(IV) .....	1430	320	58	1380	260	62	1000	210	64	710	180	59
K(IV) .....	1640	340	62	1570	320	66	1020	100	68	710	140	59
Hycar OR-25 .....	2550	260	75	—	—	—	2680	220	76	—	—	—
Hycar PA-21 .....	1370	190	69	—	—	—	380	100	54	—	—	—
Hycar OR-15 .....	2470	310	71	—	—	—	2600	210	79	—	—	—
Perbunan 26 .....	2140	550	63	—	—	—	2040	450	62	—	—	—

(a) Symbol denotes recipe and table for preparing vulcanizates. (b) Tensile strength, p.s.i. (c) Ultimate elongation, %. (d) Shore A hardness (30 sec.).

of its high volume swelling, showed the greatest decrease in tensile properties.

### Brittle Points

The most serious deficiency of Lactoprene EV vulcanizates originally developed at this Laboratory is the relatively high brittle point. This defect more than any other probably limits its utility since it restricts the number of applications where it may be employed. The use of butyl acrylate in place of ethyl acrylate as one of the co-monomers in the preparation of Lactoprene BN substantially lowers the brittle point of the vulcanizates.

Table XI summarizes the brittle point data obtained on the vulcanizates for a number of different exposure conditions as well as the initial brittle point of the unexposed samples. In addition, the brittle points of the comparative rubbers are included in the table. In the aging experiments of the Lactoprene samples at 300°F. in the air-convection oven, no significant change in the brittle points was observed in 72 hours. The Furnex-loaded stock had an initial brittle point of -11°F.; after 72 hours at 300°F., the observed brittle point was -15°F. At the end of four weeks, however, in the air-convection oven the brittle point was found to be +5°F. The Philblack O stock changed from an initial brittle point of -7°F. to +10.5°F. at the end of the four-week exposure.

The change in the brittle points of the comparative rubbers, with the exception of Hycar PA-21 which is an acrylic rubber and has a high brittle point initially, is much more pronounced. The Hycar OR-25 had a brittle point of -28.5°F. initially while at the end of 72 hours the brittle point increased to +23°F. The Hycar OR-15 had a brittle point initially of -4°F. which increased to above +36°F. in 24 hours. The Perbunan 26 rubber had initially a brittle point of -60°F. which increased to +8.5°F. in 72 hours. At 350°F. in the air-convection oven the Furnex and Philblack O stocks showed only a slight increase in the brittle point at the end of 72 hours. The brittle points of the samples aged in the various ASTM oils and the automatic transmission fluid showed a similar trend; however, the total change was not as great as in the air aging. In the oils as well the diene comparative rubbers exhibited the most pronounced change in brittle points.

Many specifications for rubber items to be used in the construction of mechanical goods require that the rubber have an extremely low brittle point. The brittle point is usually determined on the green stock which

has not been exposed to any of the conditions which the rubber sample may encounter in service. These brittle point data suggest that a rubber with a slightly higher brittle point but with superior heat and oil resistance may be far superior in performance.

### Effect of Storage of Compounded Stock

In order to expedite the evaluation of this new elastomer, the compounded stock was usually vulcanized about two hours after milling. This is not the recommended practice in rubber technology; usually, the milled stock is vulcanized 24 hours after compounding. Since this preferred technique was not followed, a study of the effect of storage on the compounded Lactoprene BN stock was not undertaken. The data in Table XII is typical of the data obtained from various storage experiments.

In these experiments, the butyl acrylate-acrylonitrile copolymer was generously supplied by the American Monomer Corporation and therefore this material was prepared under different experimental conditions from the copolymer used in the evaluation study. However, similar observations were observed with the copolymer prepared at the Government Evaluation Laboratory. The data presented in Table XII were obtained from vulcanizates prepared from the same recipe as F (III) with a curing time of 15 minutes at 300°F. for all the test samples. In all the experiments there appeared a significant lowering of the tensile strength and modulus in the first 24 hours. For the next three or four days the tensile properties remained fairly constant and then a gradual decrease of tensile properties would occur. However, no difficulty was encountered in removing the test slabs from the mold even at the end of the sixth day of storage. Storage under various humidity and

TABLE XII—EFFECT OF STORAGE OF THE COMPOUNDED STOCK ON THE TENSILE PROPERTIES OF LACTOPRENE BN-12.5 VULCANIZATES

	Time in Days				
	0	1	2	3	6
Tensile strength, p.s.i.....	1350	1190	1200	1210	1010
Elongation, % .....	640	600	630	570	690
Modulus at 300%, p.s.i.....	800	640	650	630	540
Shore A hardness (30 sec.).	48	51	46	49	48

Note: Copolymer prepared by American Monomer Corporation, Leominster, Mass. Recipe the same as F(III). 15 min. cure at 300°F.

TABLE XI—BRITTLE POINTS<sup>a</sup> (°F.) FOR LACTOPRENE BN-12.5 VULCANIZATES AND COMMERCIAL RUBBERS FOR VARIOUS EXPOSURE CONDITIONS

Sample Designation	Initial	Air-Convection Oven			Drying			ASTM No. 1			ASTM No. 2			ASTM No. 3			Commercial Automa Transm. Fluid
		1 day	3 days	28 days	1 day	3 days	at 300°F.	28 days at 300°F.	3 days at 350°F.	3 days at 300°F.	28 days at 350°F.	3 days at 300°F.	28 days at 350°F.	3 days at 300°F.	3 days at 300°F.	3 days at 300°F.	
J(II) <sup>b</sup>	-11.0	—	-15.0	+5.0	—	-9.5	-21.0	-2.2	-18.5	-2.0	-2.0	-40.0	-27.5	—	—	—	—
F(III)	-7.0	—	-9.5	+10.5	—	-2.0	-9.5	-9.5	-13.0	-13.0	-13.0	-20.0	-13.0	—	—	—	—
B(IV)	+5.0	—	+5.9	+17.5	+14.0	—	+8.5	—	+1.5	—	—	-20.0	-4.0	—	—	—	—
K(IV)	+1.5	—	-4.0	+21.0	+7.0	—	-6.0	—	-4.0	—	—	-16.5	-15.0	—	—	—	—
Hycar OR-25	-28.5	+7.0	+23.0	—	—	—	—	+10.5	—	+3.0	—	—	—	—	—	—	—
Hycar PA-21	+10.5	—	+12.0	—	—	—	—	+48.0	—	+46.5	—	—	—	—	—	—	—
Hycar OR-15	-4.0	+36.0	—	—	—	—	—	+28.5	—	+23.0	—	—	—	—	—	—	—
Perbunan 26	-60.0	-35.0	+8.5	—	—	—	—	-27.5	—	-20.0	—	—	—	—	—	—	—

(a) ASTM method of test D-746-44-T, manually operated. (b) Symbol indicates the table and recipe for preparing the vulcanizates.

temperature conditions and remilling the stock before placing it in the mold did not appear to show any significant difference in the tensile data. Furthermore, variations in the amine-sulfur ratio in the recipe or temperature of milling resulted in a similar decrease of tensile strength and modulus in the first 24 hours and these properties would then remain fairly constant for the next few days.

Another paper in preparation will describe the properties of the vulcanizates obtained from the copolymer of ethyl acrylate-acrylonitrile and another copolymer of butyl acrylate-acrylonitrile. The latter, prepared from a monomer mixture of 95% butyl acrylate and 5% acrylonitrile, results in vulcanizates with lower brittle points but greater swelling in lubricating oils than Lactoprene BN-12.5 vulcanizates.

### Summary

The data presented in this paper show that vulcanizates of Lactoprene BN-12.5, a copolymer of butyl acrylate and acrylonitrile, have certain properties superior to the vulcanizates of Lactoprene EV which was developed several years ago at this Laboratory. The Lactoprene BN vulcanizates have substantially lower volume swelling in water and lower brittle points than the vulcanizates of Lactoprene EV. Furthermore, the vulcanizates of this new rubber have outstanding resistance to dry heat, satisfactory oil resistance and low compression set. Because of these properties, Lactoprene BN-12.5 should provide improved materials for gaskets, O-rings, oil seals and similar items used in mechanical equipment.

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